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## Synthesis of phenylmagnesium carboxylates

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### Abstract

The first phenylmagnesium carboxylates,  $C_6H_5MgOOCR \cdot THF$ , have been made by reaction of phenylmagnesium bromide with the sodium salt of carboxylic acids [ $RCOONa$  {where  $R = CH_3, ClCH_2, Cl_2CH, Cl_3C, CH_3CH_2, (CH_3)_2CH, C_6H_5CH_2$  and  $CH_3(CH_2)_3CH_2$  }]. All these derivatives are white or pale yellow solids, soluble in polar solvents. The carboxylates have been characterized by elemental analysis, conductance measurements, and spectral studies ( $^1H$  NMR and IR). The IR data suggest that carboxylate group acts as a bridging bidentate ligand.

### Introduction

A number of ring opening polymerization reactions of heterocyclic compounds such as thiiranes, oxiranes, and lactones are catalysed by soluble bimetallic- $\mu$ -oxoalkoxides [ $\{MO_2Al_2(OR)_4\}$ , where  $M = Mn, Fe, Co, Ni, Cr, Zn$  and  $R = C_3H_7$  or  $C_4H_9$ ] [1–5]. We previously [6] reported the synthesis of  $MgO_2Al_2(OPr^i)_4$  by thermal condensation of magnesium acetate and aluminium isopropoxide. In order to extend these studies, we thought it of interest to prepare  $PhMgOAl(OR)_2$ . However, a survey of the literature revealed that no attempts seem to have been made to synthesize the above compound or their precursors phenylmagnesium carboxylates,  $PhMgOOCR$ . We report the synthesis of phenylmagnesium carboxylates.

### Experimental

All the reactions were carried out under nitrogen, and stringent precautions were taken to exclude moisture. Phenylmagnesium bromide and anhydrous sodium salts of carboxylic acids were prepared by reported methods [7]. The infrared spectra were recorded in KBr discs on a Perkin-Elmer 1710 FT IR spectrometer over the range  $4000-400\text{ cm}^{-1}$ . The  $^1H$  NMR spectra were recorded on a Hitachi R-600 FT spectrometer. The analyses were carried out by standard methods [8,9].

Table 1

## Characterization data

| Compound                                      | M.p.<br>(°C) | Analysis(Found<br>(calc) (%)) |                   | IR data (cm <sup>-1</sup> ) <sup>a</sup> |                  |              |
|---|--------------|-------------------------------|-------------------|--|------------------|--------------|
|   |              | Mg                            | RCOO <sup>-</sup> | $\nu_{asym}(C-O)$                        | $\nu_{sym}(C-O)$ | $\Delta\nu$  |
| PhMgOOCCH <sub>3</sub> ·THF                   | 90 (d)       | 10.4<br>(10.5)                | 25.5<br>(25.4)    | 1600<br>(1578)                           | 1425<br>(1414)   | 175<br>(164) |
| PhMgOOCCH <sub>2</sub> Cl·THF                 | 105          | 9.2<br>(9.1)                  | 35.2<br>(35.0)    | 1608<br>(1603)                           | 1420<br>(1418)   | 188<br>(185) |
| PhMgOOCCHCl <sub>2</sub> ·THF                 | 108          | 8.2<br>(8.3)                  | 43.7<br>(43.9)    | 1620<br>(1631)                           | 1370<br>(1376)   | 250<br>(255) |
| PhMgOOCCL <sub>3</sub> ·THF                   | 115          | 7.1<br>(7.2)                  | 48.3<br>(48.4)    | 1654<br>(1677)                           | 1362<br>(1353)   | 292<br>(324) |
| PhMgOOCCH <sub>2</sub> H <sub>5</sub> ·THF    | 102          | 9.7<br>(9.9)                  | 29.8<br>(29.7)    | 1580<br>(1564)                           | 1422<br>(1420)   | 158<br>(144) |
| PhMgOOCCH(CH <sub>3</sub> ) <sub>2</sub> ·THF | 116 (d)      | 9.1<br>(9.3)                  | 33.8<br>(33.4)    | 1602<br>(1572)                           | 1428<br>(1428)   | 174<br>(144) |
| PhMgOOCCH <sub>2</sub> Ph·THF                 | 132          | 7.8<br>(7.9)                  | 43.6<br>(43.8)    | 1580<br>(1560)                           | 1420<br>(1410)   | 160<br>(150) |
| PhMgOOCCH <sub>2</sub> H <sub>11</sub> ·THF   | 130 (d)      | 8.3<br>(8.5)                  | 39.8<br>(40.0)    | 1576<br>(1555)                           | 1420<br>(1415)   | 156<br>(140) |

<sup>a</sup> Values given in parentheses are those for the corresponding sodium carboxylate.

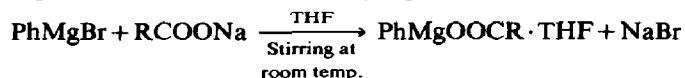
*Preparation of phenylmagnesium acetate · tetrahydrofuran (C<sub>6</sub>H<sub>5</sub>MgOOCCH<sub>3</sub> · C<sub>4</sub>H<sub>8</sub>O)*

Anhydrous sodium acetate (0.025 mol) was added to phenylmagnesium bromide (0.025 mol) in THF and the mixture was stirred at room temperature for ca. 50 h. The initially light green mixture slowly became light yellow. The precipitated sodium bromide was filtered off and weighed to check for completion of reaction. The solvent was removed from the filtrate under reduced pressure and the pale yellow solid thus obtained was recrystallised from n-hexane/THF mixture. Yield 90%. Other derivatives were made analogously. Melting point and analytical data are given in Table 1.

## Results and discussion

The chemistry of phenylmagnesium halides have been extensively studied [10] and most of the reactions involve the cleavage of the Mg–C bond rather than the Mg–X bond (X = halogen). It seemed to be advantageous to use in reactions in which the Mg–X bond is attacked instead of Mg–C bond, a reagent such as the sodium salt of carboxylic acids which contain no active hydrogen.

The reactions of phenylmagnesium bromide with sodium salts of carboxylic acids, viz. acetic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, propionic acid, isobutyric acid, phenylacetic acid, and hexanoic acid, are represented by the following equation:



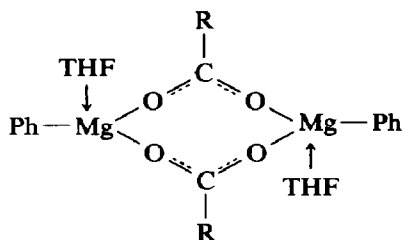
(R = CH<sub>3</sub>, ClCH<sub>2</sub>, Cl<sub>2</sub>CH, Cl<sub>3</sub>C, CH<sub>3</sub>CH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>CH, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> or CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>)

The products are white or pale yellow solids, susceptible to hydrolysis, and soluble in polar solvent such as THF, DMF and DMSO.

The more relevant IR bands of the sodium salts of the acids [11,12] and those of the magnesium compounds are listed in Table 1. Use of values of  $\Delta\nu$  to decide between bridging and chelating modes of the ligand has been described [11,13] for carboxylate systems, and a small  $\Delta\nu$  ( $\Delta\nu = \nu_{asym}(C-O) - \nu_{sym}(C-O)$ ) value found to indicate possible chelation. The high value of  $\Delta\nu$  for phenylmagnesium carboxylates ( $\Delta\nu$  values are given in Table 1) is indicative of bridging carboxylate. More recently, a new criterion has been proposed [13], according to which absorptions arising from  $CO_2^-$  deformation (at  $920-720\text{ cm}^{-1}$ ) together with a strong band at  $\sim 540\text{ cm}^{-1}$  due to  $\delta_{O,P}$ .  $CO_2^-$  are absent for the bridging mode. Since all these absorptions are absent in case of phenylmagnesium carboxylates, a bridging mode for the carboxylate ligands is favoured. The C-O-C vibrational band which appears at  $\sim 1075\text{ cm}^{-1}$  in the spectrum of THF has been shifted to  $\sim 1030\text{ cm}^{-1}$  in the solids, which indicates that THF is coordinated to magnesium in the complexes [14].

The  $^1H$  NMR spectra of each of the derivatives shows a signal at  $\sim \delta 7.4\text{ ppm}$  (m, 5H) due to phenyl group protons except in the case of the sodium phenylacetate derivative, where, as expected, integration corresponds to ten protons. The derivatives also show signals at  $\sim \delta 3.5\text{ ppm}$  (t, 4H) and  $\tau\delta 1.7\text{ ppm}$  (m, 4H) due to  $CH_2-O-CH_2$  and  $CH_2-CH_2$  protons in the tetrahydrofuran molecule. Other protons in the various derivatives resonate at the same positions as in the corresponding sodium salts.

The conductance measurement showed that all the derivatives are nonelectrolytes in DMF. On the basis of above studies following structure is tentatively proposed.



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